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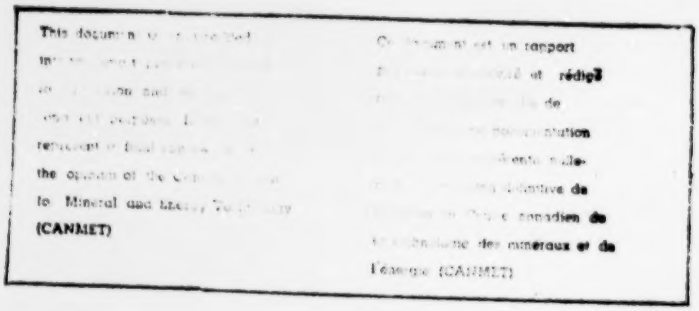

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SYNTHESIS OF BETA"-ALUMINA BY SPRAY DRYING

by

T.A. Wheat* and B. Kindl**

ABSTRACT

A simple spray-drying process is reported for the synthesis of precursor powders that will readily convert during sintering to the single-phase, beta"-alumina that is required for use in various energy storage and conversion systems such as the Na-S battery.

The process exploits the use of spray drying as a practical means of homogeneously dispersing the reagents throughout the bulk of a reactive, commercially available alumina powder. The low cost and simplicity of the process make it potentially attractive for commercial exploitation.

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INTRODUCTION

In the early 1970's, a major R&D program was initiated by the Ford Motor Company, Dearborn, together with Rensselaer Polytechnique and the University of Utah to develop the sodium-sulphur battery for electric vehicle purposes. That program, which was funded by the National Science Foundation, was undoubtedly the stimulus for the flurry of activity in the 1970's in researching and developing the various aspects of this battery system. As a result, industrial programs were started elsewhere in the United States (notably by General Electric Co.) as well as in Europe (Brown Boveri, Germany; Chloride Silent Power and British Rail, U.K.; Companie Generale d'Electricite, France) and in Japan (Yuasu).

By the mid 1970's, it had become widely recognised that two forms of a beta-alumina solid electrolyte occurred in the soda-alumina system and that one (beta") had a significantly higher conductivity than the other (beta). Further, it was shown that the meta-stable beta"-form could be stabilized by the presence of low concentrations of either lithia (Ford Motor Co) or magnesia (Chloride Silent Power and British Rail) and that extended annealing was required to produce material having a high beta" content (e.g., ~1720K for 8 h).

By the time the CANMET program was initiated in 1976, it had proved extremely difficult to produce material having significant concentrations of the beta"-phase. Consequently, the initial emphasis of the CANMET program was to develop material having 100% beta"-alumina, which could be used to establish the intrinsic characteristics of this phase. Despite statements in the literature at that time that the two phases must probably always co-exist, the first single-phase beta"-alumina was produced in the CANMET laboratories in 1977 (1,2). However, the process that was exploited depended on the very rapid freezing of an aqueous spray containing dissolved reagents followed by the freeze drying of the frozen particles. Although suitable for research purposes, this process is quite slow and presently unsuitable for the industrial production of large batches of material.

Of the various techniques that are available for the synthesis of homogenous and reactive ceramic raw materials (3), spray drying has been used for many years by the ceramic industry as a simple, low-cost unit process that yields a very uniform material that is required for subsequent use in automatic forming equipment. For that reason, CANMET and others have been

studying this unit process as the practical means of producing the beta" phase that lends itself to exploitation by industry.

EXPERIMENTAL PROCEDURE

Previous work has been conducted in CANMET to synthesize the beta" phase by spray drying an aqueous solution containing Al, Na and either Li or Mg stabilizers as either the sulphates or nitrates (4). However, those processes were unsuitable because the product either formed a liquid phase between ~500 and 700K of the calcination stage (nitrates) or they formed thin, hollow glass-like balls during spray drying (sulphates) producing a morphology that, despite a subsequent milling stage, was quite unsuitable for compaction and subsequent densification during conventional sintering. The reagents also suffered a very high mass loss during the calcination and decomposition of the raw material (over 80 mass % loss for the sulphates) that resulted in a very low yield of the final product. Attempts to minimize this problem by using concentrated feed solutions to the drier failed. Clearly, it was necessary to further increase the concentration of the feed such that the solubility limit of even the most soluble component would be exceeded and hence slurries would have to be used. As the molar composition of beta"-alumina typically lies in the range 1:5 to 1:8 soda:alumina, the mass ratio of alumina to the other components is ~9:1, i.e., provided the main component was present as a finely divided solid phase in the drier feed, then high concentrations of reagents could be used in the slurry feed and the problem of high mass loss on calcination would be avoided.

Raw Materials Selection

It was decided that an aqueous slurry would be used instead of some of the alcohol-based slurries that have been used elsewhere as this would use the cheapest liquid and would avoid any consideration of liquid recovery downstream of the drier. In addition, it was desirable to use a common anion for the soluble salts (to avoid possible eutectic formation and inhomogeneity occurring during calcination) and to also use salts that suffer the least mass loss on decomposition. A final requirement was that the anion should decompose cleanly and directly to the oxide on heating. This last point precluded the selection of oxalates, formates, acetates and citrates as they

send to yield a low concentration of carbon in powder mixtures, especially in the presence of a high surface area solid upon which the solutes are commonly adsorbed.

From the above criteria, the carbonate would appear to be an ideal choice but, unfortunately, $MgCO_3$ is essentially insoluble (0.01 mass % in cold water). By comparison, the bicarbonate is much more soluble in water when saturated with CO_2 - ~20 g/L at room temperature (5). Consequently, this was the anion selected for the present work.

The selection of the commercial alumina was based on availability, low cost, high reactivity and high purity (Ca and K have been shown to seriously degrade the final product in service). As the cost of specialty ceramic raw materials can rise above $50/kg, the balance between cost, reactivity and purity is important. So far, no attempt has been made to optimize the process with respect to the alumina raw material. From these criteria, it was decided to use Reynolds RC 172 DBM raw material. Table I gives some of the characteristics of the material.

In common with the other well-dispersed, fine-grained Bayer-processed aluminas produced by dry ball milling (DBM), an approximately 0.1 mass % residue of an organic additive used as a dry milling deflocculant can be detected in the as-received material. For this reason, the alumina was ignited to 720K for 8 hours prior to use.

TABLE 1: Properties of RC-172 alumina as specified by manufacturer

Average Particle Size:	0.65 micrometres
Typical Chemical Analysis:	99.7% alumina 0.04% soda 0.07% silica 0.03% ferric oxide balance principally magnesia
Green Pressed Density at 5000 psi:	2230 kg/m^3
Fired Density at 1785K with a 2 h Soak:	3900 kg/m^3
Firing Shrinkage:	17.0%

Preparation of Slurry

The feed material for spray drying was composed of a suspension of alpha-alumina in water containing dissolved sodium and magnesium bicarbonates. Initially, the overall composition selected for this work was $0.8MgO:Na_2O:5Al_2O_3$ after the work of Farrington and Briant (6); however, as this resulted in the formation of sodium aluminate (which could be detected in the X-ray diffraction powder patterns, Fig. 3A) the composition was modified to include more alumina, resulting in the composition $0.8MgO:Na_2O:6Al_2O_3$. This composition has been examined by others (7-10).

For the purposes of examining this spray-drying process on a laboratory scale, small batches of nominally 30 g each were prepared, dried and further processed. The opportunity to work successfully with such small quantities of material was afforded by the use of a recently developed bench-top spray drier which uses an all-glass system, Fig. 1.

Initially, a magnesium bicarbonate solution was prepared by dissolving 5 g of the basic carbonate in 600 mL of distilled water through which CO_2 was slowly bubbled until a clear solution was obtained - approximately 90% dissolved in 3 h. A double salt solution was then prepared by adding 7.5 g of $NaHCO_3$ to 410 mL of the magnesium bicarbonate solution, which was constantly stirred while CO_2 was bubbled through the mixture until a clear solution was again obtained. Finally, 26.9 g of ignited RC 172 alumina was added to the constantly stirred bicarbonate solution through which CO_2 was gently bubbled prior to drying.

The conditions for spray drying are given in Table II. Because the alumina component was agglomerated in the slurry, it was necessary to use an automatic, intermittently operated nozzle cleaner in the spray jet to prevent permanent plugging. The rate of cleaning was about once per second.

TABLE II: Conditions for spray drying the slurry

Equipment Settings	Operating Conditions
heater 14.5 aspirator 9	inlet temp 483K outlet temp 390K
pump 8	slurry feed rate 8 mL/min
atomizer* air pressure 50 psi air flow 600	atomizing air flow rate of 600 L/h

* Using a 0.5 mm diameter pneumatic nozzle

Calcination and Sintering

The dried powder was subsequently calcined for 45 min in air between 1473K and 1673K in a covered Pt dish to decompose the bicarbonates and fully react the material, forming a mixture of beta- and beta"-alumina. Because the product had an unusually low bulk density at this stage, and would not sinter to much above 77% relative density, it was necessary to increase the density of the particles used to form the green discs. This was done by first milling the as-calcined powders using an alumina pestle and mortar (to minimize significant contamination: on a commercial scale an alumina-lined mix muller would be ideal), followed by uniaxially pressing the powder to 280 MPa (40 000 psi), then hand milling again in an attempt to form dense particles having a size distribution suitable for dense packing. The powder was finally formed into green discs measuring 1.27 cm in diameter and 2-3 mm in thickness under a pressure of 140 MPa using 0.7 g of calcined material. Controlled experiments demonstrated the importance of the initial milling stage prior to the first pressing operation - failure to mill at this point results in a reduction of the relative density of sintered material to the range 85-90%.

The green discs were sintered either in air or buried in loose powder of the same composition contained in a Pt crucible hvaing a loosely fitting lid. Samples were sintered for 90 min at 1873K.

RESULTS AND DISCUSSION

Density

Although the major component in the system was a commercial alpha-alumina which had a tap density of 1300 kg/m^3, the spray-dried product was very light having a tap density of only 200 kg/m^3. The value increased slightly with increasing calcination temperature. However, even at 1673K the tap density was only 225 kg/m^3. Use of these as-calcined powders resulted in compacts having a sintered relative density of only ~90%, suggesting that the agglomerates in the powder prior to pressing were either of too low a density or had a size distribution that resulted in poor packing (or both).

After milling and the initial pressing stage, the green-pressed density of the compacts was ~2000 kg/m^3 - a slight increase in density with the calcination temperature was noted. Because the initial pressing pressure was 280 MPa and the final forming pressure was 140 MPa, there was little increase in green density after the second pressing. However, after sintering the milled and re-pressed material, the compacts had a consistently high density but, because of their small size and the associated low accuracy in measuring the bulk density of $\pm$ 50 kg/m^3, it was not possible to determine the influence of calcination temperature on the final density. The data are shown in Fig. 2.

X-ray Diffraction Analysis

Calcined Powders

Samples of the calcined powder were examined using standard X-ray diffraction (XRD) techniques to determine the identity of the phases formed as a function of temperature. An estimate of the phase ratio beta:beta" was made by comparing the intensity of the (1,0,7) peak of the beta phase (occurring at 39.01 degrees 2θ using Co K-alpha) with that of the (0,1,11) peak of the beta" phase (occurring at 40.27 degrees 2θ) from which the parameter f(beta) was calculated:

$$f(\text{beta}) = I(\text{beta})/\{I(\text{beta}) + I(\text{beta}")\}$$

As the intensities of these two peaks are approximately equal in the calculated diffraction patterns of the pure phases (4), the ratio can be regarded as an approximation of the phase ratio in any mixture. Clearly, a

value of zero is required for this parameter as such material would be essentially 100% of the higher conducting beta" phase.

Table III shows the phases formed at each temperature and the value of the f(beta) parameter. It can be seen that temperatures above 1473K are required to ensure that only a beta-beta" mixture is formed in the powders: below that temperature, the powder pattern shows a moderately well crystallized $NaAlO_2$ phase with a very weak pattern of beta- and /or beta"-alumina. It is for this reason that an estimate of the f(beta) parameter is difficult for the lower temperature calcines - hence the character "?" appears in Table III. Figure 4 shows the XRD patterns obtained for these calcines.

TABLE III: Analysis of powders calcined at temperatures (K) shown

	1473	1523	1573	1623	1673
Phase	$NaAlO_2$ + vw b/b"	b/b"	b/b"	b/b"	b/b"
f(beta)	?	?	?	0.60?	0.31

Sintered Material

After firing, the patterns are well resolved indicating that the material is well crystallized. Only in the case of sintered material produced from powder calcined at 1473 and 1523K can any trace of the beta phase be detected in any part of the pattern and even in these cases the value for f(beta) was ~0.05. The XRD patterns obtained from the flat surface of the **solid** sintered samples are shown in Fig. 4.

Optical Microscopy

Samples produced from material calcined at each temperature were mounted and polished using conventional techniques to examine the microstructure in reflected light, the result is shown in Fig. 5. It can be seen that the material is free of large voids but, when viewed under high power it is seen to have very fine residual porosity. An attempt to show this porosity has been made in the inset of Fig. 5: in the actual samples it is seen that the porosity is always located at the boundaries of the

lath-shaped crystals of the beta"-alumina. The absence of porosity in the centre of the grains is surprising in view of the high heating rate of about 300K/min used to fire the materials.

CONCLUSIONS

It has been demonstrated that a reactive precursor powder for the formation of beta"-alumina can be produced using a commercially available alumina powder and the industrially acceptable process of spray drying an aqueous slurry (instead of the alcoholic slurries used elsewhere). This avoids any need to consider solvent recovery systems downstream of the drier.

It has also been demonstrated that, by using appropriate processing conditions, these powders can be formed into sintered material of single-phase beta"-alumina having over 98% relative density when fired in a covered container for only 90 min.

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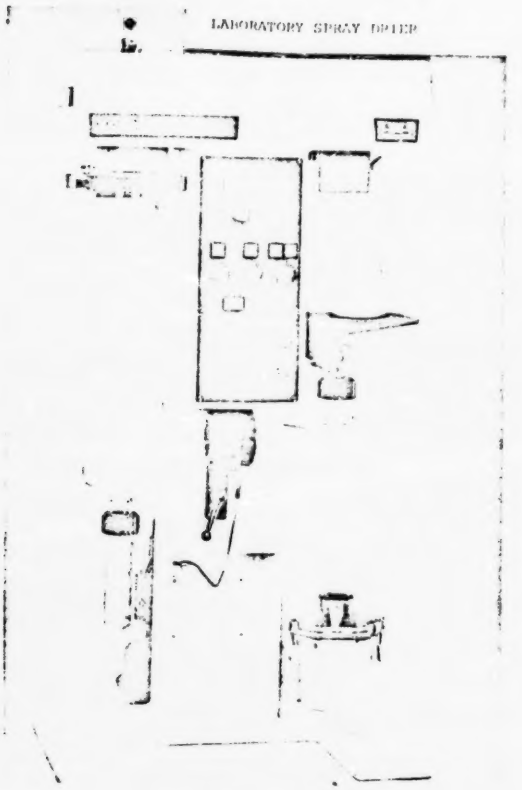


Fig. 1 - View of bench-top spray drier used in present work.

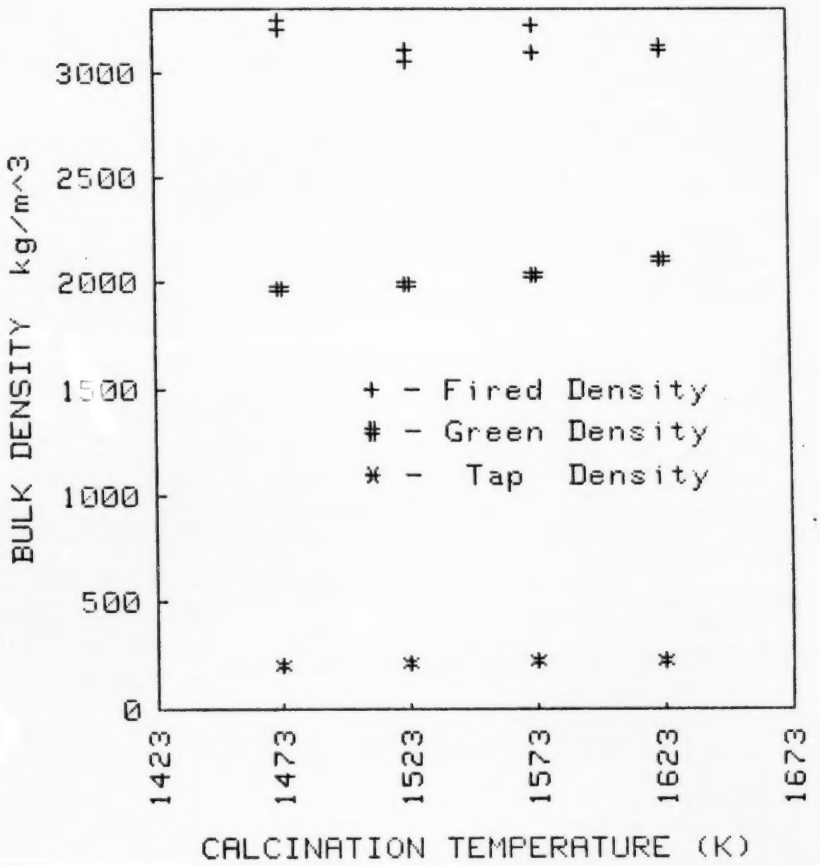


Fig. 2 - Variation of density of product at various stages of processing as a function of calcination temperature.

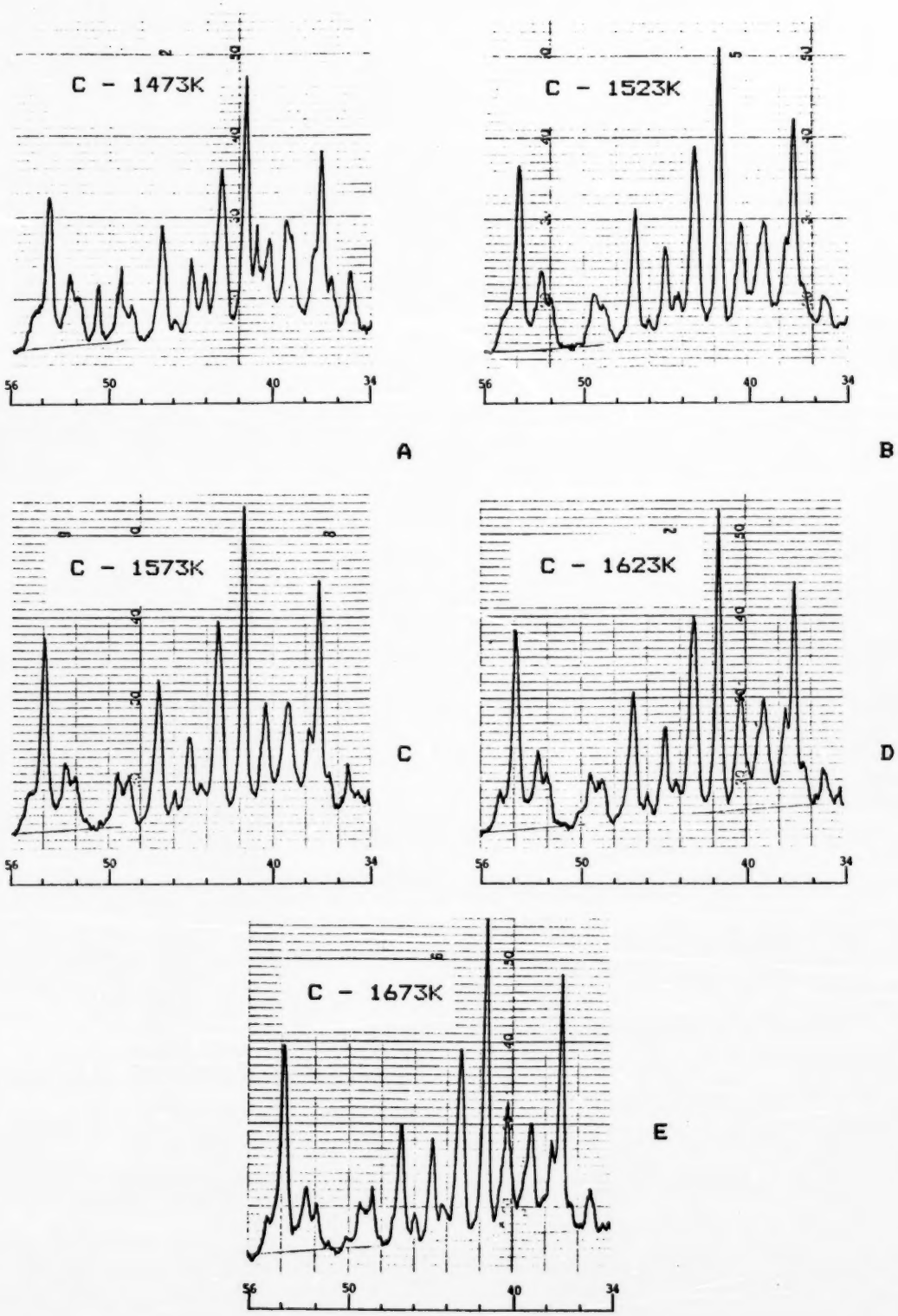


Fig. 3 - XRD powder patterns of material calcined in air for 45 min at temperatures shown. Scale indicates 2θ (Co K-alpha).

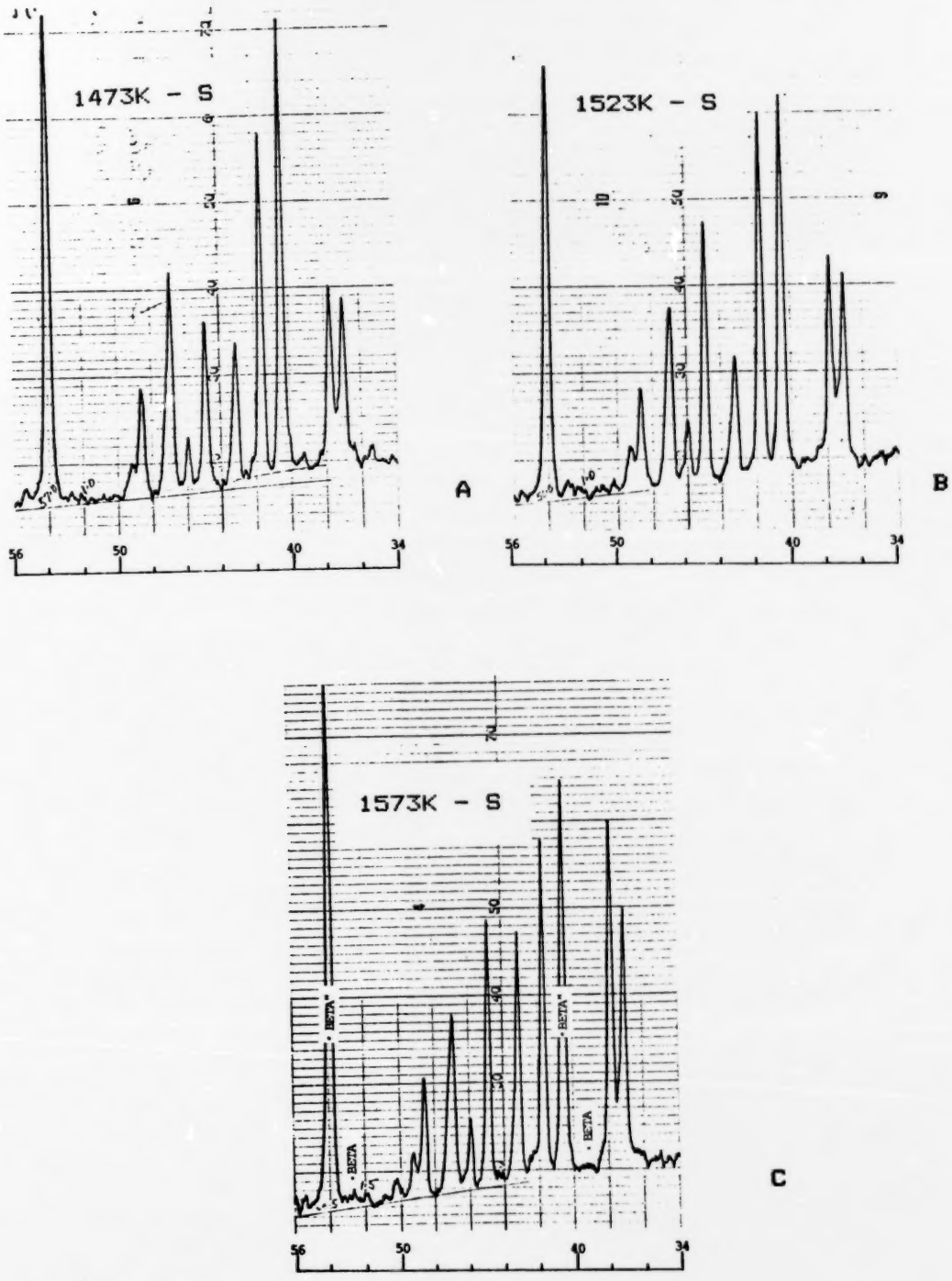
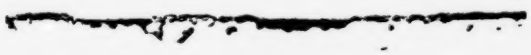


Fig. 4 - XRD patterns of the surface of sintered discs. Scale indicates 2θ (Co K-alpha). Peaks at 40 degrees used to calculate f(beta) are indicated in 4(C).

1473 K

1523 K



1623 K

500 μm

Fig. 5 - Optical micrographs of material sintered for 45 min at the temperatures indicated (x50). Inset x500.